

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the production of Aqueous Polyurethane Dispersions

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organized under the laws of Germany, of 509, Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of aqueous polyurethane dispersions.

Polyurethane plastics are known in which organosilicon compounds are concurrently used in the preparation thereof. The preparation is carried out by incorporating a polysiloxane into the polyurethane composition in a kneading machine, an internal mixer or a mixing roller. Processes in which polysiloxanes containing reactive hydrogen atoms, through which they are incorporated by isocyanate polyaddition into the polyurethane are apparently more advantageous. The polysiloxane grouping of the polyurethanes which have been modified in this way has a protective action against hydrolytic influences. The stabilising action against the influence of moisture is particularly apparent in polyurethanes formed from polyesters. It is also already known to produce opaque polyurethanes with the concurrent use of polysiloxanes.

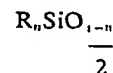
The process so far known for the production of polyurethane plastics, in the preparation of which polysiloxanes are concurrently used, are limited to the production of polyurethane compositions which are processed either from the melt while shaping or with the aid of the machines normally used in the injection moulding art, or by pressing, extruding or granulating, or they can be spread or sprayed from organic solution.

The present invention provides a process

for the production of an aqueous polyurethane dispersion wherein at least one polyisocyanate is reacted with at least one polyhydroxy compound with a molecular weight of from 300 to 20,000 and 0.05% to 300% by weight, advantageously 0.1% to 30% by weight, based on the polyhydroxy compound, of at least one polysiloxane with reactive hydrogen atoms and a molecular weight of from 194 to 20,000 optionally together with a chain extender with reactive hydrogen atoms, water being added to the reaction mixture or to one of the components thereof to form the dispersion.

In the aqueous polysiloxane-modified polyurethane dispersions obtained in this way, the chemical incorporation of the polysiloxane into the polyurethane results in the organosilicon groups being set in the polyurethane in such a way that a migration, exuding or extraction of the polysiloxane from the polyurethane composition, or from the films, filaments, foils and two-dimensional structures obtainable therefrom, or a phase separation of the dispersion with "fish eye" formation is substantially prevented. Due to the polysiloxane modification, the polyurethane plastics are especially pliable. The concurrent use of small quantities of polysiloxanes is sufficient to impart a pleasing, soft, full and warm handle to the polyurethane coatings obtained therefrom.

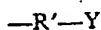
The polysiloxanes with reactive hydrogen atoms which are concurrently used according to the invention correspond to the general summation formula



(I.)

in which R represents an optionally neutrally substituted aliphatic, cycloaliphatic or aromatic hydrocarbon radical, advantageously methyl or phenyl, while n has a value greater than 1 and is at the most 3.

At least once in the molecule, R is a carbon-functional organic radical, to which the grouping



(II)

can generally be attributed, wherein R' is a divalent aliphatic hydrocarbon radical with from 1 to 6 carbon atoms, which can be interrupted by ether groups or by thioether groups, and Y is, for example, a hydroxyl, mercapto or carboxyl group or a primary or secondary amino group.

Such carbofunctional radicals include, for example:

Hydroxymethyl	$-\text{CH}_2\text{OH}$
Hydroxybutyl	$-(\text{CH}_2)_4\text{OH}$
β -Hydroxyethyl-oxymethyl	$-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$
β -Hydroxyethyl-mercaptomethyl	$-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{OH}$
β,γ -Dihydroxypropyl-mercaptomethyl	$-\text{CH}_2-\text{S}-\text{CH}_2-\text{CHOH}-\text{CH}_2\text{OH}$
Mercaptomethyl	$-\text{CH}_2\text{SH}$
β -Mercaptoethyl-mercaptomethyl	$-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{SH}$
β -Carboxyethyl	$-\text{CH}_2-\text{CH}_2-\text{COOH}$
Aminomethyl	$-\text{CH}_2-\text{NH}_2$
α -Aminobutyl	$-(\text{CH}_2)_4-\text{NH}_2$
n -Butylaminomethyl	$-\text{CH}_2-\text{NH}-\text{C}_4\text{H}_9$

The organopolysiloxanes which are to be used according to the invention are obtainable by conventional methods. Thus, for example, the especially suitable hydroxymethyl polysiloxanes can be prepared by the direct reaction of bromomethyl polysiloxanes with an alcoholic caustic potash solution. 4-Aminobutyl polysiloxanes are prepared by hydrogenation of the readily available nitriles and corresponding carboxyl derivatives are obtained by saponification of the cyanoalkyl-silicon compounds.

Aminomethylsiloxanes are obtained by amination of the halomethylsilicon compounds with ammonia or primary amines.

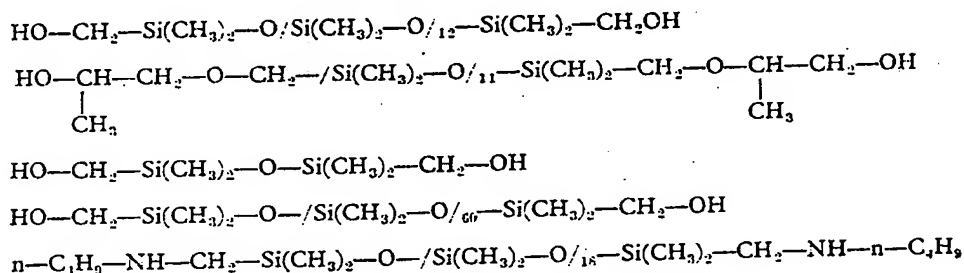
In many cases, the functional groups are

initially introduced into siloxanes of low molecular weight; the products thus obtained are then transformed by a conventional equilibration reaction into polysiloxanes of high molecular weight.

Polysiloxanes with a molecular weight of from 500 to 6000 are preferred. Furthermore, substantially linear polysiloxanes and these with terminal hydroxyl or amine groups are desirable.

Such polysiloxanes are already described in French Specification No. 1,291,937 and in German Auslegeschrift No. 1,114,632.

Thus, for example, the following polysiloxanes are suitable:



The proportions in which the components are used can vary within wide limits, depending on whether it is desired to produce soft, flexible or elastic or very hard plastics.

5 In the last-mentioned case, the quantity of the compound with reactive hydrogen atoms having a molecular weight of from 300 to 20,000, does not have to be more than 10% of the polyurethane composition, but it can also be smaller. The molecular weight of the polyhydroxyl compound to be used may be between 300 and 20,000 advantageously from 800 to 4000. Low molecular weights are particularly preferred for hard materials.

15 Polysiloxane-modified polyurethane dispersions with solid contents of from 10% to 60% by weight are preferably used, and polyurethanes which exist in the form of dispersions may also contain incorporated salt groups.

20 Examples relating to the production of polyurethane dispersions, in the preparation of which the polysiloxanes used according to the invention can be concurrently employed, are found in German Auslegeschrift Nos. 1,187,012, 1,184,946, 1,178,586, 1,179,363, in Belgian Specification Nos. 653,223 and 658,026 in Specification No. 883,568, in French Specification No. 1,108,785, in U.S. Specification No. 3,178,310 and in Polymer Preprints 6 (1965), No. 1, pages 156 to 162 and in French Patent No. 1,496,584.

25 In the production of the polyurethane dispersions obtainable according to the invention, a pre-polymer containing isocyanate groups is generally prepared initially from the compound with reactive hydrogen atoms and a molecular weight of from 300 to 20,000, the polysiloxane to be used according to the invention and having reactive hydrogen atoms with a molecular weight of from 194 to 20,000, the polyisocyanate and the chain extender optionally concurrently used. The prepolymer in organic solution, optionally in the presence of emulsifiers and basic chain extenders, is dispersed in water, or, conversely, water-containing emulsifiers are added with dispersion formation and the organic solvent may be removed. In the preparation of dispersions of polysiloxane-modified polyurethanes which contain salt groups, these groups being defined according to the Belgian Specification No. 653,223 and the contents of the salt groups varying from 0.05% to 10% by weight, advantageously from 0.1% to 3% by weight, based on the polyurethane composition, the prepolymer containing isocyanate groups can be reacted in organic solution with a salt-like component or a component capable of forming a salt and, optionally, water is added after the groups capable of forming a salt have been transformed to the salt form and the organic solvent has been distilled off. In principle, the converse procedure can also be used, in which water, optionally containing the salt-

like components or the component necessary for the salt formation, is initially provided, and the pre-polymer containing isocyanate groups or the polyurethane with groups capable of forming a salt is incorporated by stirring.

Salt-like components or components capable of forming a salt and suitable for incorporation are, for example, taurine, methyl- 75 taurine, tartaric acid, glycine, lysine, 6-amino-caproic acid, diaminobenzoic acid, hydrazinodisulphonic acid, lactic acid, an adduct of unsaturated acids, cyclic dicarboxylic anhydrides, lactones, sultones, cyclic sulphates with aliphatic and aromatic diamines, triamines, diaminols or amine diols, and also the hydrogenated adducts of unsaturated nitriles, e.g. that of acrylonitrile with an amino acid such as glycine or taurine and their salts, and also methyl diethanolamine, *n* - butyl- 85 diisopropanolamine, 1,3 - di - amino - N,N-dimethylaminopropane and bis - (N,N - γ aminopropyl)methylamine. Examples of the salt-forming components which react with the groups capable of forming a salt so that a salt is formed are also contained in Belgian Specification No. 653,223.

90 Dispersions of polysiloxane-modified polyurethane can also be produced by a subsequent reaction of known polysiloxane-modified polyurethanes with substances which impart a salt character to the polysiloxane-modified polyurethane composition, for example, with sultones, lactones, cyclic sulphates and dicarboxylic anhydrides. In one particular form of the invention, the groups capable of forming salts are only partially transformed into salt form, so that there are still free groups which are not transformed into salt form. Due to the proportion of the free, for example, acid groups in relation to the groups transformed to salt form, it is thus possible by the law of mass effect to adjust the pH initially to a desired value.

105 Aqueous dispersions of polysiloxane-modified polyurethanes containing salt-like groups can also be obtained by the compound with reactive hydrogen atoms with a molecular weight of from 300 to 20,000 and/or the polysiloxanes to be concurrently used according to the invention and having reactive hydrogen atoms with a molecular weight of from 300 to 20,000 containing salt-like groups or groups capable of forming a salt.

110 The aqueous polysiloxane-modified polyurethane dispersions are stable, capable of being stored and despatched and can be transformed according to the invention into foils, films, filaments or two-dimensional structures. The separation of the polysiloxane-modified polyurethane compositions from the dispersions is effected by coagulation or removal of the water by evaporation, possibly at a relatively high temperature, clear, transparent or opaque plastics with thermoplastic or elastic 125 130

properties being obtained, depending upon the composition.

For this purpose, the dispersions are, for example, applied by means of a spray pistol or a doctor blade to the substrates, such as natural or artificial leather, paper or textile webs, which are to be coated or impregnated and dried at room temperature or at 80° C to 160° C., possibly in the presence of cross-linking agents.

To give the handle of cotton and staple rayon materials, the dispersions are preferably applied by padding. After condensation with hexamethylolmelaminemethylether, and ammonium chloride for five minutes at 150° C,

soft and pleasing handle effects are produced, for example, by the use of the dispersion described in Example 1.

Furthermore, it can be shown that the dispersions generally improve the wet crease-recovery angle of the finishes. For this purpose, cotton poplin is treated by padding, the solution used containing 50 g/litre of solid substance of the dispersion, 120 g. of dimethylurea dimethylether and 10 g/litre of magnesium chloride. The fabric is dried and condensed for five minutes at 150° C. The wet crease-recovery angles established are set out as follows:

	Wet crease-recovery angle		Dry crease-recovery angle	
	K	S	K	S
Unfinished fabric	67	77	48	61
Fabric finished with the dispersion of Example 1	129	139	170	170
Dispersion of Example 2	138	134	155	168

K = Warp. S = Woof.

The resistance to abrasion of fabrics finished with the dispersions according to the invention is also favourably influenced. Thus,

a cotton poplin finished with the dispersion described in Example 1 shows the following abrasion values:

	Revolutions
Blank test	200
Fabric finished with dispersion of Example 1	250

Coated papers show a matt, silk-like surface lustre, a coating composition adjusted to be whitish and opaque produces a uniform matt coating which covers unevennesses and coloured irregularities in the substrate.

The conversion to foils, films, filaments or two-dimensional structures can also be carried out in the presence of conventional cross-linking agents. For this purpose, polyfunctional substances with a cross-linking action are added during the preparation of the dispersion or to the prepared dispersion, which substances cause a chemical cross-linking after evaporation of the water at room temperature or at a higher temperature. Sulphur, sulphur sols, formaldehyde, substances which yield or act in the manner of formaldehyde, polymethylol compounds of melamines, ureas

and dicyandiamide or their methyl or butyl ethers, soluble phenol formaldehyde, urea formaldehyde or melamine formaldehyde reaction products, epoxide compounds, e.g. the polyglycidyl ethers of polyhydric alcohols such as ethylene glycol, diethylene glycol, glycerine and sorbitol, free and partially or completely masked polyisocyanates, carbodiimides, polyamines, polyacids, polyhalides, compounds of divalent and polyvalent metals, such as dioxides, carbonates and hydroxides of calcium, zinc and magnesium, organic and inorganic peroxides may be mentioned, for example. Finally, fillers, plasticisers, pigments, hydrofluoric and salicylic acid sols, aluminium, clay and asbestos dispersions can be incorporated into the polysiloxane-modified polyurethane dispersions, by being added during

the preparation of the dispersion or to the finished dispersion.

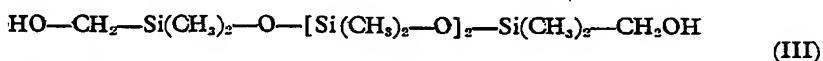
The dispersions can be blended with similarly charged dispersions, for example, with polyvinylchloride, polyethylene, polystyrene, polybutadiene, copolymer-plastic dispersions and pure polysiloxane emulsions.

The products of the process show a good resistance to water, oil and chemical cleaning and impart a soft and full handle, especially to textiles. At relatively high temperatures, for

example above 150° C., the products of the process are stabilised against yellowing.

EXAMPLE 1

105.3 G of adipic acid - 1,6 - hexanediol-neopentylglycolpolyester (molar ratio 30:22:12; OH No. 66.6) are dehydrated for 30 minutes at 120° C/12 mm Hg. and thereafter, 78.7 g of a polysiloxane of the average formula:



with an OH content of 2.7% and 55.0 g. of 1,6-hexanediisocyanate are added and the mixture is reacted for two hours at 120° C. at 60° C, the melt is taken up in 800 ml. of acetone and a mixture of 7.52 g. of 1,2-ethylenediamine, 15.25 g. of 1,3-propanesultone and 70 ml. of a 10% potassium hydroxide solution in 50 ml. of water are added. After completion of the reaction, 480 ml. of water are introduced. When the reaction mixture has become homogeneous, the water is distilled off. A stable, white dispersion with a solid content of 39.0% and a pH value of 6 is obtained. The dispersion dries into elastic opaque coatings, with pleasing handle effects. The dispersion is stable with respect to a 10% aqueous sodium chloride solution. Coagulation occurs when hydrochloric acid is added. A polyurethane dispersion prepared without the concurrent use of the above polysiloxane dried into clear coatings of a comparatively hard and cold handle.

EXAMPLE 2

A pre-polymer is prepared from 202.0 g. of adipic acid - 1,6 - hexanediol - neopentylglycol polyester (molar ratio 30:22:12; OH No. 65.85), 7.9 g. of the polysiloxane compound of Example 1 and 38.0 g. of 1,6-hexanediisocyanate, as in Example 1, and this is taken up in 700 ml. of acetone after having been cooled to 60° C. A mixture of 3.76 g. of 1,2 - ethylenediamine, 7.63 g. of 1,3-propane - sultone and 25 ml. of a 10% sodium hydroxide solution in 50 ml. of water is added to the solution in acetone, and 425 ml. of water are stirred into the resulting mixture. Stirring of the mixture is continued until the streaks which form have disappeared. After the acetone has been distilled off, a purely aqueous 40% white dispersion is obtained, which dried to form slightly opaque, water-resistant foils. The foils have a pleasing, soft and warm-handle.

EXAMPLE 3

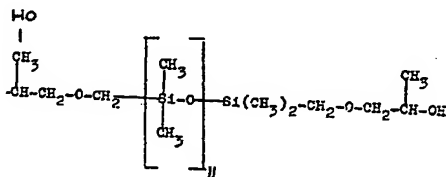
105.3 G. of adipic acid - 1,6 - hexanediol-neopentylglycol polyester (molar ratio 30:22:12; OH No. 66.6), 78.7 g. of the

polysiloxane compound of Example 1 and 42.0 g. of 1,6 - hexanediisocyanate are reacted for two hours at 120° C. The viscous melt is taken up at 60° C. in 600 ml. of acetone and slowly stirred into a solution of 18.1 g. of bis - (N,N - γ aminopropyl)methylamine in 600 ml. of acetone.

After 30 minutes, the mixture is heated from 55° C. to 60° C and 11.6 g of dimethylsulphate are added. After the addition of 550 ml. of water, the acetone is distilled off. The dispersion obtained is a 35% dispersion and has a good compatability with dilute acids.

EXAMPLE 4

250 G. of the adipic acid - 1,6 - hexanediol - neopentylglycol polyester (OH No. 60) referred to in Example 3 are melted and intimately mixed with 2.5 cc. of polysiloxane of the general formula



175 G. of tolylenediisocyanate (isomer mixture 65:35) are then added at room temperature, and the batch is heated to 80° C and left for 30 minutes at this temperature. 50 G of butanediol and 30 g. of N-methyldiethanolamine in 300 cc. of acetone are added to the melt at 30° C. After being stirred for 2½ hours at 55° C, the melt is diluted with 400 cc. of acetone and stirred for another three hours. The 48% acetone solution has a viscosity of 117 stokes.

400 G. of this solution are alkylated with 8.8 cc. of dimethylsulphate at 50° C, and diluted with 10 cc. of water, and 200 cc. of acetone and 400 cc. of water are successively added. After the acetone has been distilled off, a 33.6% aqueous colloid polyurethane

solution is obtained which is of ointment-like consistency. On drying, silky lustrous coatings are obtained which have a pleasing handle and a good fastness to light.

- 5 A comparison test conducted without adding polysiloxane leads under the same conditions to a thin colloidal solution, which dries into crystal clear, highly lustrous coatings having a comparatively cold handle. As well as the handle effect, a reduction in the
10 colloid particle size is also obtained by incorporation of the siloxane.

EXAMPLE 5

- The procedure of Example 4 is followed,
15 but the 8.8 cc. of dimethylsulphate are replaced by only 4.4 cc. of dimethylsulphate (49% of the theoretical quantity) and also 2 cc. of glacial acetic acid are added after alkylation. Results comparable with those of
20 Example 4 are obtained, but the thickening effect is only slight.

EXAMPLE 6

- 250 G. of the polyester of Example 4 are melted and intimately mixed with 5.0 cc. of
25 the polysiloxane of Example 4. 272 G. of tolylenediisocyanate are then added at room temperature, whereupon the mixture is heated to 80° C. and left at this temperature for 30 minutes. 100 G. of butanediol and 30 g.
30 of N-methyldiethanolamine in 400 cc. of acetone are added to the melt at 30° C.

After stirring for three hours at 55° C, the melt is diluted with 500 cc. of acetone and stirred for another hour.

- 35 6.5 cc. of dimethyl sulphate are added to 750 g. of this 48% polyurethane solution and 40 cc. of water, followed by 3.8 cc. of glacial

acetic acid and 560 cc. of water, are slowly added at 50° C. The acetone is then distilled off. A 42% latex is obtained which dried
40 into delustered silky, hard, water-resistant and light-fast coatings. The coatings have a soft, pleasing, silky handle.

Products produced by way of comparison without the addition of the polysiloxane are
45 of high lustre and have a cold handle.

WHAT WE CLAIM IS:—

1. A process for the production of an aqueous polyurethane dispersion wherein a polyisocyanate is reacted with a polyhydroxy compound having a molecular weight of from
50 300 to 20,000 together with from 0.05% to 300% by weight calculated on the polyhydroxy compound of a polysiloxane with reactive hydrogen atoms and with a molecular weight of from 194 to 20,000 optionally
55 together with a chain extender with reactive hydrogen atoms, water being added to the reaction mixture or to one of the components thereof to form the dispersion.

2. A process as claimed in claim 1 substantially as herein described with reference
60 to any of the specific examples.

3. Aqueous polyurethane dispersions when produced from a process as claimed in claim
65 1 or 2.

4. Foils, films filaments and two-dimensional structures when made by shaping from a dispersion as claimed in claim 3.

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